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(54) Catalysts for Smoking Products or Filters Therefor

(57) Catalysts are described that have particularly good activity when used in smoking products, or filters for smoking products, for oxidising carbon monoxide to carbon dioxide, which comprise a support carrying a catalytically active metal or compound

and which have a defined activity. The catalyst may include mixtures of tin or tin compound with other catalytic material. The catalysts may involve a redox mechanism. Particularly valuable results are obtained when a redox catalyst is made by first depositing a major amount of one component of the catalyst and then a minor amount of the other component.

SPECIFICATION Smoking Products

Upon smoking a smoking product, such as a cigarette, carbon monoxide is formed at and near the burning tip and a gaseous mixture containing carbon monoxide is drawn through the mouth end of the cigarette. The proportion of carbon monoxide depends, inter alia, on the air supply through the walls of and along the length of the 10 smoking product. By increasing the air supply the proportion of carbon monoxide can be reduced but even with optimum air supply the gas will still contain a significant proportion of carbon monoxide.

It is known to include absorbents, generally in 15 a filter tip, to absorb physically some of the carbon monoxide but these do not remove sufficient. It is also known to include, generally in a filter tip, catalysts or oxidants to oxidise carbon 20 monoxide to carbon dioxide. There is a discussion of various oxidants and catalysts for this purpose in publication FTR5 by J. W. Reynolds from Eastman Chemical Products Inc., entitled "Results of Experimental Work to Remove CO from a 25 Mixture of O, and N, by use of Modified Cigarette Filters".

Many of the materials discussed in that report are based on hopcalite, which contains copper oxide and manganese dioxide and is thus an 30 oxidant rather than a catalyst but catalysts such as palladium on molecular sieve were also tested. The report concluded that all the tested materials were unsatisfactory. Thus even at 80°C hopcalite only removed 60% of the carbon monoxide in the 35 tests described and was deactivated by water while other catalysts were less sensitive to water but were even less effective at removing carbon monoxide. For instance 0.5% palladium on molecular sieve was stated to remove only 2% 40 carbon monoxide in the test described.

A smoking product or filter for a smoking product according to a first aspect of the invention comprises a catalyst for low temperature oxidation of carbon monoxide to 45 carbon dioxide and which comprises a support carrying at least one catalytically active metal, present as the metal or a metal compound, and which has an activity at 25°C of 60 to 100% after 10 puffs of a test gas mixture, as herein defined.

50 The defined activity is determined by forming a gas mixture of 3% CO, 10% CO₂, 13% O₂ and 74% N₂ and puffing this over 500 mg of the catalyst being tested and analysing the resultant gas mixture and hence determining the 55 conversion of carbon monoxide, each puff constituting 35 ml of the gas mixture at atmospheric pressure and being passed for two seconds over the catalyst at the rate of one puff per minute. Preferably the catalyst has an activity 60 of from 60 to 100% after 20 puffs and most preferably after 30 puffs, and in particular it preferably has an activity substantially of 100% after 10 puffs. Since activity tends to decrease with usage, all catalysts according to the

65 invention inevitably will have an activity of greater than 60%, and generally 100%, after 3 puffs whereas the greatest activity described in the article by Reynolds was 50% after 3 puffs, and most activities were much less, for example 2% 70 for palladium on molecular sieve.

According to a second aspect of the invention a smoking product or filter comprising a catalyst which has an activity at 25°C of from 50 to 100% after 3 puffs and 30 to 100% after 10 puffs of a 75 tobacco smoke vapour phase as herein defined. This activity is determined in the same manner as the activity of the gas mixture but the smoke mixture used is tobacco smoke and contains moisture. Preferably the catalyst used in smoking 80 products or filters according to the invention has both this activity on the smoke mixture and also the defined activity on the test gas mixture.

The metal is generally selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, 85 osmium, platinum, chromium, rhenium, tungsten and tip. In many embodiments of the invention it is present as the metal but some metals, e.g. tin, may be present as oxide or other compound while in others, especially those involving a redox 90 mechanism and described below, the metals will be in ionic or salt form.

We have found a number of independent steps which when used in the preparation of catalysts comprising a support and catalytically active 95 metal or metal compound give a very useful improvement in activity over that obtainable by traditional methods and which when used together give particularly satisfactory results. Thus the described steps may be used individually 100 or in any compatible combination thereof.

In one step a catalyst is made by generating in

a hydroxyl containing solid support material surfaces activated by having a deficiency of hydroxyl groups and contacting the activated 105 surfaces while still activated with a solution of a substance providing catalytically active material. These hydroxyl deficient surfaces can be made by heating the support material but preferably are made by crushing pellets of the support material. 110 A preferred process comprises heating the support material to a temperature of at least 20°C above the temperature at which expulsion of chemisorbed water is substantially completed but below the temperature at which substantial 115 degradation of the support material occurs and impregnating the support while still activated. In one method the material that is heated is in the form of powder having a particle size of less than 50 microns whilst in another method the heating 120 is conducted substantially immediately prior to or during the manufacture of pellets of support material, and the activated surfaces are subsequently generated by crushing the pellets. The contact of the activated surfaces with the 125 catalytically active material or the substance providing it should be made while the surfaces are still activated, that is to say before substantial deactivation occurs, as would happen if they were

left exposed to the atmosphere for several days.

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Generally contact is within 3 hours of generating the active surfaces.

When the active surfaces are generated by crushing, it seems that the active form was generated during initial manufacture of the pellets and was trapped within and protected from ageing influences by the outer layers of the pellets, and the surfaces are exposed by the crushing.

Heating steps used for activation generally involve heating at between 300 and 800°C, most preferably between 400 and 650°C, especially 500 to 600°C, particularly when the support is a zeolite or alumina. The removal of chemisorbed 15 water and subsequent creation of a deficiency of hydroxyl groups can be observed by differential thermal analysis. The heating is best conducted by calcining in air or nitrogen for a period that can be determined by routine experimentation, usually 20 from 6 to 24 hours. More details of this method are described in our Belgian and German applications entitled "Catalysts" (and which claims priority from British Application No. 2391/78), and the entire disclosure of which is 25 incorporated herein by reference.

Another way of improving activity arises from the method of impregnating the support with the catalytically active material. Traditional methods have used a wholly aqueous solution of the 30 substance providing the catalytically active material or, in rare instances, a wholly organic solution. In the invention improved activity is obtained when a microporous support material is impregnated with a solution of a substance 35 providing the catalytically active material in a mixture of water and an organic liquid that reduces the surface tension of the solution. In a simple method the solvent may be a 50/50 mixture of water and methanol. Broadly, best 40 results are obtained when the organic liquid constitutes 10 to 90% preferably 50 to 80%, by volume of the mixture, is inert to the catalytically active material, reduces the hydrogen bonding within the solution and between the solution and 45 the support, and is wholly miscible with the water in the solution. Often it is preferred that it has

molecular dimensions smaller than the pore size of the support material. Preferred organic liquids are selected from alcohols and cyclic ethers, in 50 particular being selected from tetrahydrofuran, methanol, ethanol, dioxan and furan, methanol generally being preferred. They are generally aliphatic or alicyclic. More details of this method are described in our Belgian and German 55 applications No. entitled "Catalysts" (and which claim priority from inter alia the complete specification of British application No. 23257/78) and the entire disclosure of which is incorporated herein by reference.

Another way of improving activity of the catalyst comprises impregnating the support material with the substance providing the catalytically active material in anionic form instead of the more usual cationic form. This is of 65 particular value when the support material has

been activated by dehydroxylation and when impregnation involves physical adsorption of the substance into the material, instead of the more usual ion exchange. Thus contact between the 70 solution and the support is preferably maintained while at least some, for example 50 to 100%, of the solvent evaporates, this being particularly preferred when the catalytic material is in anionic form.

Another way of improving activity comprises 75 selection of the manner of reducing the catalytically active material that is deposited on the support. Various methods of reduction are known and can be used but best activity seems to 80 be obtained for low temperature catalysts, as are required in the invention, when the reduction is by carbon monoxide.

A preferred method of making a catalyst for use in the invention comprises starting with a 85 zeolite, for example 3A, 4A, 5A, 10X or 13X (4A, 5A or 13X being preferred) dehydroxylating this to activate it, physically absorbing a solution (in water and an organic liquid that reduces the surface tension of the solution) of the catalytically 90 active material in anionic form, at least partially evaporating the solvent, and reducing the catalyst by carbon monoxide.

Preferably the catalyst comprises a microporous support having a pore diameter below 30 Å and carrying a catalytically active material deposited predominantly within the pores. The diameter is preferably less than 16 Å. The diameter is preferably at least 4 A. Preferably the amount of catalytically active metal or metal 100 compound deposited within these micropores is at least 0.1% of the total weight and often it is deposited atomically dispersed within the pores. It seems that previous catalysts proposed for smoking products, such as the catalysts discussed 105 in the article by Reynolds, had little or no catalytic material deposited within any micropores in the catalytic support. Instead most at least of the catalyst metal was probably deposited on the outer exposed surfaces of the support in relatively 110 thick and non-uniform layers.

By depositing the catalytic metal in the described mono-layer fashion within the described microporous structure not only is good activity obtained but also poisoning by large 115 molecules such as tar molecules is prevented, the microporous structure acting as a physical filter to prevent such poisoning.

The metals that may be used as the catalyst, or as the metallic component of a catalytically active 120 compound, can be selected from all the metals known to be useful as oxidation catalysts and include transition metals, most preferably of Groups 6, 7 and 8 noble metals being particularly preferred. Preferred metals are iron, cobalt, nickel, 125 ruthenium, rhodium, palladium, osmium, platinum, chromium, rhenium and tungsten, and also tin. Particularly preferred are catalysts containing platinum, palladium, rhodium, rhenium and tin. However, particularly desirable results are 130 obtained when mixtures of metals are used,

especially mixtures of platinum or palladium with rhodium, rhenium or tin. Especially preferred are catalysts based on platinum or palladium or palladium and rhodium, together with tin. While 5 palladium or platinum are generally present in metallic form the tin may be present as stannous oxide. Such catalysts have more stable activity in the presence of moisture.

According to a third aspect of the invention a 10 smoking product or a filter for a smoking product comprises a catalyst for low temperature oxidation of carbon monoxide to carbon dioxide which comprises a support carrying tin which may be present as the metal or a metal compound, and 15 at least one other metal selected from noble metals, transition metals and metals of Groups 6, 7 and 8 and which may be present as metal or metal compound. Preferably this other metal is selected from platinum, iron, cobalt, nickel, 20 ruthenium, rhodium, osmium, chromium, rhenium and tungsten. Most preferably the support carries palladium or a compound thereof and tin or a compound thereof, and optionally other catalytic materials. Such catalysts may be carried on 25 supports such as those described above and in the cross-referenced applications.

All the described catalysts have surprisingly good activity in the presence of moisture but particularly satisfactory results are obtainable if 30 the catalyst is one that functions by a redox mechanism that involves reaction with water. Thus a smoking product of filter for a smoking product according to a fourth embodiment of the invention comprises a support carrying 35 catalytically active materials that will effect the low temperature oxidation of carbon monoxide to carbon dioxide by a redox mechanism that involves reaction with water.

Such a catalyst involves first and second redox 40 components. The first (e.g. a palladium or other noble metal compound) catalytically oxides the carbon monoxide and is reversibly reduced in the reaction. The second (e.g. a copper salt) then serves as an oxidising agent to reoxidise the first 45 component back to a catalytically active state and is reversibly reduced in the reaction. The second is then reoxidized to a state in which it is able to oxidise the first component again. In the catalysts used in this fourth embodiment of the Invention at 50 least one of these three reactions involves reaction with moisture with the result that the overall redox system does not function at all, or functions with very low activity, in a wholly anhydrous environment.

Redox catalysts used in solution, i.e. in the liquid phase without a support, and which operate by this general mechanism are well known and are often referred to as Wacker catalysts and redox catalysts that are carried on a support and function by this mechanism are also known and are used commercially for, for instance, the production of vinyl acetate. Such catalysts are described in, for instance, British Patent
Specification No. 976,613, US Patent
Specification No. 3,300,528 and pages 46 to 57

of Chemical Economy and Engineering Review
November 1972 Volume 4 No. 11 to all of which
reference should be made for full disclosure of the
first and second components and the entire
disclosure of which is incorporated herein by
reference.

Although the first component is usually of a noble metal such as palladium any metal that is capable of catalytically oxidising carbon monoxide to carbon dioxide while entering into the necessary redox reaction can be used. Similarly although the second component is generally provided by a metal (as a salt) again any compound that can undergo the necessary redox reaction can be used. It is usually a metal compound, for example a salt of copper, tin or iron, but it can be an organic compound, for instance a quinone such as benzoquinone.

The second component normally is one that
has a low redox potential in the system, for
instance below 1 and usually below 0.5, e.g. 0.05
to 0.3 volts. Particularly good results have been
obtained using copper salts or tin salts or
mixtures thereof as the second component,
especially when the first component is a
palladium compound.

The first and second components may be present in any form that permits them to enter into the necessary redox reactions. The second 95 component is preferably such as to provide a metal in cationic form and thus a salt with any suitable anion, for example halide (generally chloride), sulphate or nitrate may be used. The first component may be introduced in the cationic 100 form, e.g. Pd²⁺ (usually as PdCl₂) but preferably is anionic, for instance PdCl₄⁻².

The amount of the first component is always less than the amount of the second component and generally is less than 50% of the weight of the second component. For instance it may be 5 to 20% by weight of the second component. Typically the amount of first component is 0.1 to 0.5% while the amount of second component is 1 to 10%, usually 2 to 7% by weight of the total catalyst. The second component may be provided by more than one material in which event the materials used preferably have similar redox potentials. One of the materials of the second component may be present in a minor amount, 115 e.g. similar to the amount of the first component, while the other is generally present in a larger

The first and second components are carried on a support which may be macroporous or microporous but best results are obtained when it is microporous, having a pore size of 30 Å or less, generally 4 to 16 Å. While charcoal, for instance coconut charcoal which has been partially oxidised by air heating at about 500°C in order to activate it, and alumina may be used more highly microporous supports such as zeolites, e.g. zeolite 13X, are preferred.

The first and second components may be deposited on the support in known manner but 130 best results are obtained if the catalyst is made by

substantially saturating the surfaces of the support with some or all of the second component (or a compound capable of providing the second component upon heating) and then 5 depositing the minor amount of the first component (or a compound capable of providing the first component upon heating). Thus a redox catalyst made by this method constitutes a further aspect of the invention. Such a redox 10 catalyst is of particular value for the low temperature oxidation of carbon monoxide to carbon dioxide in smoking products or filters for smoking products but can also be used in any environment where a redox catalyst is required, 15 for instance in the production vinyl acetate or in a catalytic converter for an automobile exhaust.

Although successive deposition of the components of the catalyst is mentioned in column 2 of US Patent Specification 3,300,528 it

10 has not previously been appreciated that very beneficial results, particularly for catalysts intended for low temperature oxidation of carbon monoxide, can be obtained if the support surfaces are initially substantially saturated with the promoter and then only a minor amount of the noble metal is deposited.

The second component, or at least the major proportion of it, is preferably a metal salt and saturation of the support surfaces with it may be achieved by impregnating the support with a solution of the salt, permitting ion exchange to occur, removing excess liquid and then repeating the process at least one and usually more, e.g. 3 to 6 times, and finally washing the catalyst and drying it.

The solution should not be too concentrated as otherwise the activity may be impaired, and generally has a concentration of below 50 g/l, preferably 20 to 40 g/l. The solvent is generally 40 water.

The first component may be introduced as a solution in any suitable solvent, preferably a substantially non-aqueous solvent. Methanol and dichloromethane are particularly suitable as the solvent or as components of the solvent. Minor amounts of other second components, for example stannic chloride, may be introduced in this solution. The support is then dried.

Best activity occurs if the support is then beated at moderate temperatures for half to 4 hours, generally under ambient atmospheric conditions. Temperatures of 100 to 200°C for about 2 hours are generally satisfactory.

One preferred redox system includes
55 compounds of palladium and copper and
optionally tin. Another includes compounds of
manganese (generally as the second component)
and cerium.

The described catalysts are normally in powder form, e.g. below 50 microns, and may be distributed through smoking products or included in a filter for a smoking product. Preferably they are included in a filter. The filter may be a triple filter, with catalytic powder, either by itself or mixed with absorbant and the product of the p

a central component between fibrous end portions. The powder may be loose or may be bonded into a porous plug. The powder may also be bonded to fibres that form the central portion
70 of a triple filter or that are distributed throughout some or all of any filter construction or may be bonded to a sheet which is crumpled or spirally wound to form part or all of a filter.

The following are examples of catalysts
75 suitable for use in smoking products of the invention.

Example 1

13X zeolite pellets containing clay binder and having a particle size of 1.5 to 3 mm were ground in a domestic grinder and were then sieved to leave a fraction having a particle size of 30 to 60 mesh. Within 1 hour three grams of this powder was mixed with 20 ml water containing 0.75 ml chloroplatinic acid solution (5% w/v) (i.e. an aqueous solution containing 750 ppm platinum). The mixture was left for 12 hours at about 40° C by which time the solution had evaporated to dryness to leave a free-flowing powder.

Example 2

90 The method of Example 1 is repeated except that contact between the solution and the powder is maintained for, for instance, 10 hours, preferably under reflux, and excess solution is then decanted and the wet powder evaporated to 95 dryness.

Example 3

The method of Example 1 is repeated except that the solution is a 50% water—50% methanol solution and reduction is by formaldehyde.

100 Example 4

The method of Example 2 is repeated except that the powdered zeolite is first contacted with stannous or stannic ions and after drying is then contacted with chloroplatinic acid of the same or similar concentration.

After drying, the products of each of Examples 1 to 4 are reduced by carbon monoxide at 350°C. All these catalysts have exceptionally good

activity for use in smoking products and
preferably are incorporated in filters in the manner
described above. In particular they all had an
activity of 100% after 10 puffs of a gas mixture as
described above and an activity of above 30%
after 10 puffs of a smoke mixture containing tars.

To demonstrate the increase in activity obtainable independently by each of the various steps described above a number of further experiments were conducted. In each of these activity was determined on a gas mixture of CO,
 CO₂, O₂ and M₂ by the method described above.

Experiment 1

in a filter for a smoking product. Preferably they are included in a filter. The filter may be a triple filter, with catalytic powder, either by itself or mixed with absorbents such as granular carbon, in 125

Aged zeolite 13X molecular sieve was preheated to various temperatures for various times and was then contacted with sufficient of an aqueous solution of chloroplatinic acid to

deposit 2% platinum. When the preheating was at temperatures of below 400°C the activity was found to be less than about 20%. However when preheating was conducted at temperatures above 400°C over night a rapid increase in activity was observed, with a value of about 70% at temperatures of 500 to 600°C and a value of about 100% at a temperature of 580°C when a similar support was preheated at 580°C for 5 days immediately prior to deposition of the platinum, it was found to have an activity of 100% after 20 puffs and 80% after 30 puffs.

Experiment 2

In a separate experiment, zeolite 13X had 2%
platinum deposited in it as chloroplatinic acid and the catalyst was then reduced by heating at 350°C. When reduction was conducted for 3 hours using hydrogen the activity was 53%, whilst when it was conducted for 2 hours with hydrogen followed by one hour with carbon monoxide the activity was about 80% whilst when all the reduction was with carbon monoxide, for 3 hours, the activity was 100%, and was still 100% after 20 puffs and was 90% after 25 30 puffs.

Experiment 3

In a separate series of experiments on the effect of altering reduction conditions a support zeolite 13X containing 1% platinum was reduced 30 with carbon monoxide for 3 hours at temperatures of between 150 and 450°C. Best results were obtained at temperatures of from 250 to 400°C, with the optimum activity being obtained at a temperature of 350°C.

35 Experiment 4

13X zeolite pellets were crushed and sieved as in Example 1, and then impregnated with various solutions of chloroplatinic acid sufficient to give 0.5% platinum. When the volume of solution was 40 5 ml and the solvent was solely water the activity was 75 whilst in a parallel experiment when the volume was 10 ml and the solvent was a mixture of equal parts water and methanol the activity was 100% after 10 puffs and 73% after 20 puffs.

45 Example 5

Zeolite 4A powder is heated at a temperature of about 580°C to activate it, and impregnated with chloroplatinic acid solution in equal parts of water and methanol. It was left for 12 hours at 50 about 40°C by which time the solution had evaporated to dryness to leave a free flowing powder. The platinum was then reduced by carbon monoxide at 350°C. Like the products of Examples 1 to 4, the resultant catalyst had good 55 activity and was preferably incorporated in a filter in the manner described above.

Example 6

Zeolite 13X was immersed in an aqueous solution of 30 g/l cupric chloride, left to soak in 60 that solution to permit ion exchange to occur and

was then separated from the remaining solution. The separated product was then immersed in fresh solution and the whole process repeated until it had been given five immersions. Analysis showed at that time that the catalyst contained from 5 to 6% copper based on the dry weight. The product was then washed with water and dried. It was then immersed in a solution of equal parts methanol and methylene dichloride containing about 0.5% Na₂PdCl₄ and 0.5% stannic chloride, both measured as metal. The product is dried at room temperature and is then heated at 150°C for 2 hours while exposed to the ambient atmosphere.

75 The resultant catalyst has an activity of about 85% in the smoke mixture test described above and an activity at least as high as this on the synthetic test mixture test described above.

Claims

- 1. A smoking product or filter for a smoking product comprising a catalyst for low temperature oxidation of carbon monoxide to carbon dioxide which comprises a support carrying at least one catalytically active metal, present as the metal or a metal compound, and which has an activity at 25°C of 60 to 100% after ten puffs of a test mixture, as herein defined.
 - 2. A smoking product or filter for a smoking product comprising a catalyst for low temperature oxidation of carbon monoxide to carbon dioxide and which comprises a support carrying at least one catalytically active metal, present as the metal or a metal compound, and which has an activity at 25°C of from 50 to 100% after three puffs and 30 to 100% after ten puffs of a smoke mixture containing tars as herein defined.
- A smoking product or filter according to claim 1 or claim 2 comprising at least one catalytically active metal, that may be present as
 the metal or a metal compound, selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, platinum, chromium, rhenium, tungsten and tin.
- 4. A smoking product or filter for a smoking product according to claim 1 or claim 2 comprising as the catalytically active metal, that may be present as metal or metal compound, both tin and a metal selected from platinum and palladium.
- 110 5. A smoking product or filter for a smoking product comprising a catalyst for low temperature oxidation of carbon monoxide to carbon dioxide which comprises a support carrying tin, that may be present as the metal or a compound, and at
- 115 least one other metal selected from noble metals, transition metals and metals of Groups 6, 7 and 8 and that may be present as metal or metal compound.
- 6. A smoking product or filter for a smoking product according to claim 5 in which the other metal is selected from platinum, iron, cobalt, nickel, ruthenium, rhodium, osmium, chromium, rhenium and tungsten.
 - 7. A smoking product or filter for a smoking

product according to claim 5 comprising palladium or a compound of palladium and tin or a compound of tin.

8. A smoking product or filter for a smoking product according to any preceding claim in which the support is a microporous support having a pore diameter of less than 30 Å.

9. A smoking product or filter for a smoking product according to any preceding claim in 10 which the support comprises a zeolite or alumina.

- 10. A smoking product or filter for a smoking product according to any preceding claim in which the catalyst has been made by depositing a compound of catalytically active metal within the 15 support and then reducing the compound by carbon monoxide.
- 11. A smoking product or filter for a smoking product according to any preceding claim in which the catalyst has been made by depositing a 20 compound of catalytically active metal within the support by impregnating the support with a solution of the compound in a mixture of water and an organic liquid that reduces the surface tension of the solution.
- 25 12. A smoking product of filter for a smoking product according to claim 11 in which the solution is made up of from 50 to 80% methanol and 50 to 20% water.
- 13. A smoking product or filter for a smoking 30 product according to any preceding claim in which the support is a hydroxyl containing support and the catalyst has been made by providing activated surfaces having a deficiency of hydroxyl groups and contacting the activated 35 surfaces while thus activated with a solution of a compound of catalytically active metal.

14. A smoking product or a filter for a smoking product according to claim 13 in which the support is activated by crushing pellets of the 40 support and contacting the crushed support with the solution while activated.

15. A smoking product or a filter for a smoking product comprising a catalyst for low temperature oxidation of carbon monoxide to carbon dioxide 45 and which comprises a support carrying catalytically active materials that will cause low temperature catalytic oxidation of carbon monoxide to carbon dioxide by a redox mechanism that involves water.

16. A smoking product or a filter for a smoking product according to claim 15 in which the catalytically active materials comprise palladium or a compound thereof and tin or a compound thereof.

55 17. A smoking product or filter for a smoking product according to claim 15 or claim 16 in which the support is a microporous support having a pore diameter of less than 30 Å.

18. A smoking product or a filter for a smoking

60 product according to any preceding claim additionally comprising, as a catalytically active metal, copper or a compound thereof.

19. A redox catalyst suitable for low temperature oxidation of carbon monoxide to 65 carbon dioxide comprising a support, a first redox component for catalytically oxidising the carbon monoxide and a second redox component for oxidising the first component, wherein the catalyst has been made by substantially

70 saturating the surfaces of the support with some or all of the second component or with a compound capable of providing the second component upon heating, and then depositing a minor amount of the first component or a

75 compound capable of providing the first component upon heating.

20. A catalyst according to claim 19 in which the second component is a metal compound and the surfaces of the support are saturated with some or all of the second component by impregnating the support with a solution of a salt

of the metal and permitting ion exchange to occur, removing excess liquid, and repeating the impregnation at least once.

85 21. A catalyst according to claim 20 in which the solution has a concentration of 20 to 40 g/l.

- 22. A catalyst according to any of claims 19 to 21 in which the first component is a metal compound and is introduced into the support as a 90 solution of a compound of the metal in a substantially non-aqueous solvent.
 - 23. A catalyst according to claim 22 in which the solvent comprises methanol and/or dichloromethane.
- 95 24. A catalyst according to any of claims 20 to 23 in which the support is microporous having a pore diameter of less than 30 Å.
- 25. A catalyst according to any of claims 19 to 24 in which the second component comprises a 100 major amount of a compound of a metal and a minor amount of a compound of another metal and in which the metal providing the said minor amount is deposited onto the support with the first component. 105
 - 26. A catalyst according to any of claims 19 to 25 in which the first component comprises a noble metal compound and a second component comprises a compound of a metal selected from copper and tin.

110 27. A catalyst according to any of claims 19 to 26 comprising a palladium compound and a copper compound.

28. A catalyst according to claim 27 additionally comprising tin or a compound 115

29. A smoking product or filter for a smoking product comprising a catalyst according to any of claims 19 to 28.

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